CHEMICAL STRUCTURE OF COAL TAR DURING DEVOLATILIZATION

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Introduction

Enormous progress has been made in coal pyrolysis research during the last two decades. Models of coal devolatilization have progressed from simple rate expressions based on total mass release[1, 2] to empirical relationships based on the elemental composition of the parent coal[3] to models that attempt to describe the macromolecular network of the coal.[4-6] In the last several years, advancements in chemical analysis techniques have allowed quantitative investigations of the chemical structure of both coal and its pyrolysis products, including the nature of the resulting char. A prominent research goal is to accurately predict the rates, yields, and products of devolatilization from measurements of the parent coal structure. The prediction of nitrogen species evolved during devolatilization is of current interest. These goals necessitate modeling the reaction processes on the molecular scale, with activation energies that relate to chemical bond breaking rather than to the mass of products released from the coal. Solid-state ^{13}C NMR spectroscopy has proven particularly useful in obtaining average values of chemical structure features of coal and char, while liquid phase ^{1}H NMR spectroscopy has been used to determine some of the chemical features of coal tar.[7-10] Pyridine extract residues from coal and partially-pyrolyzed coal chars have also been analyzed by solid-state ^{13}C NMR spectroscopy, and the extracts have been analyzed by ^{1}H NMR spectroscopy.[11]

Several current devolatilization models use some kind of network approach to describe the parent coal structure and subsequent devolatilization behavior.[4-6] Coal is modeled as an array of aromatic clusters connected by labile bridges. Kinetic expressions are postulated for the rate of bridge scission, and statistical representations are used to determine the number of clusters liberated from the coal matrix as a function of the number of bridges cleaved. The vapor pressure of liberated clusters are calculated and used to determine yields of tar versus metaplast. Crosslinking reactions eventually connect the remaining metaplast to the char matrix. Such models require knowledge of the average size of the aromatic clusters in the coal, the number of attachments (bridges and side chains) per cluster, the ratio of bridges to side chains, and the average size of the bridges or side chains. Several reviews of these models have been published.[12, 13] All three of these models use the solid-state ^{13}C NMR data to some extent to guide selection of coal-dependent input parameters to describe the coal matrix. One model demonstrated success in using the solid-state ^{13}C NMR data directly as the only coal-dependent structural input parameters.[6] One of the common assumptions in these models is that the aromatic clusters are not broken during the pyrolysis process, and hence the bridge breaking rate largely controls the devolatilization rate. Therefore, the average number of aromatic carbons per cluster in the coal is equal to that in the char and in the tar.

In a recent paper, Niksa[14] postulated that nitrogen evolution during pyrolysis could be modeled assuming that the mass of nitrogen per aromatic cluster in the coal tar was equal to that in the parent coal. A theoretical analysis was performed using tar data reported in the literature to determine the validity of Niksa's assumption. Elemental analyses of tar samples were reported by Freihaut, et al.[15, 16] and by Chen.[17] It has been shown that the carbon aromaticity of the pristine tar (as estimated from ^{1}H NMR spectroscopy) is similar to that of the parent coal for both lignites and bituminous coals .[8, 9] Assuming that the number of aromatic carbons per cluster in the tar is equal to that in the coal, the mass of nitrogen per cluster $M^{N}_{cluster}$ can be calculated as follows:

$$M^{N}_{cluster} = \frac{x_N}{x_C} MW_C \frac{C_{cl}}{f_{a'}} = MW_{cl}\, x_N \qquad (1)$$

where x_N = wt% N in coal (daf), x_C = wt% C in coal (daf), MW_C = molecular weight of carbon, C_{cl} = # of aromatic carbon per cluster, $f_{a'}$ = carbon aromaticity, and MW_{cl} = molecular weight per aromatic cluster. Results of this analysis are shown in Fig. 1, indicating that the mass of nitrogen per cluster in the tars do not equal the mass of nitrogen per cluster in the parent coal. The results shown in Fig. 1 are pieced together from data reported in several experiments, which may have caused errors. It may also be possible that (a) the number of aromatic clusters in the tar does not equal that in the coal, or that (b) the carbon aromaticity of the tar does not equal that of the coal. This paper describes experiments and analyses of *one* set of coal tars and chars. This is the first time that this high resolution ^{13}C NMR spectroscopy techniquw has been applied to coal tars, and data regarding the number of aromatic carbons per cluster and carbon aromaticities in coal tars are presented.

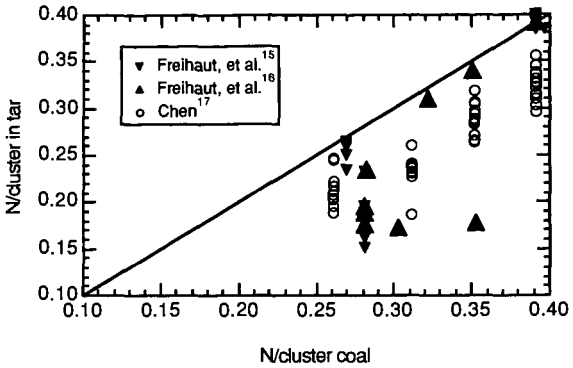

Figure 1. Comparison of the calculated nitrogen per cluster in the tar and in the parent coal.

Experimental Apparatus

Samples of tar and char were produced at atmospheric pressure in the High Pressure Controlled-Profile (HPCP) drop tube reactor.[18] The HPCP drop tube furnace is a laminar flow furnace with a computer-controlled wall temperature profile to create isothermal conditions for reactivity tests. Particles are fed with the primary gas through a water-cooled injector, which can be moved in order to vary particle residence times. The secondary gas flows into a preheater prior to entering the reactor. Wall heaters control the temperature profile in the drop tube furnace. The collection probe collects the entire mass flow and quenches all particle reactions. The collection probe is water-cooled with gas quench jets in the probe tip. A permeable liner inside the main probe tube allows quench gas to be injected radially along the length of the probe to reduce particle and tar deposition. A virtual impactor follows the collection probe to aerodynamically separate the gases from the heavier particles. A cyclone separates char particles from tars and aerosols, and the tars and aerosols are eventually collected on filters.

Table I
Coal Properties

Coal	PSOC ID	Rank	%C (daf)	%H (daf)	%N (daf)	%Ash (dry)
Illinois #6 (IL)	1493D	hvc bituminous	77	5.0	1.5	15.1
Blue #1 (NM)	1445D	sub-bituminous	77	5.7	1.3	3.6
Pittsburgh #8 (PA)	1451D	hva bituminous	84	5.5	1.7	4.1

The HPCP was used to pyrolyze coal samples in 100% nitrogen, at moderate gas temperatures of 930 K, and at residence times of 230 ms and 420 ms. Relatively low temperatures were used in these experiments to minimize possible secondary reactions in the evolved coal tars. Properties of the three coals examined are shown in Table 1. The 63-75 μm size fraction was used in all of these experiments, resulting in heating rates of approximately 10^4 K/s. The "D" on the Penn State coal identification number signifies coals from a suite selected by the DOE Pittsburgh Energy Technology Center's Direct Utilization/AR&TD program. These coals have been well characterized and studied by many other researchers, including those referenced in Figure 1.

^{13}C NMR Analysis

Solid state ^{13}C NMR techniques (CP/MAS and dipolar dephasing) have been used to determine the chemical structure features of coals and coal chars.[7, 19] In addition to carbon aromaticity ($f_{a'}$), the distinction between aromatic carbons with and without attachments (such as hydrogen, carbon, or oxygen) is measured. The specification of the number of aromatic carbons per cluster (C_{cl})[7] provides the basis for the determination of many interesting chemical structure features. Probably one of the most useful quantities is the number of attachments per aromatic cluster, referred to as the coordination number (σ+1).

A high resolution ^{13}C NMR technique was recently developed and applied to model compounds, mixtures, and coal-derived liquid samples.[20] This technique uses spin-lattice relaxation to differentiate protonated from nonprotonated carbons, based on relaxation differences

arising from direct CH dipolar interactions. Average aromatic ring sizes and other lattice parameters are estimated using the procedures used for solid-state ^{13}C NMR.[7, 19]

Tar samples were dissolved in deuterated methylene chloride (CD_2Cl_2) and then filtered. A significant amount of residue was obtained for each tar. This tar residue was subsequently analyzed using the CP/MAS and dipolar dephasing solid-state ^{13}C NMR technique in the same fashion as that used for coal char.

Results and Discussion

Tars collected at 230 ms were analyzed using the ^{13}C NMR spin-lattice relaxation technique; data are presented in Tables 2 and 3. Data for char collected at 420 ms are also presented in Table 2. Analysis of the dissolved tar from the Illinois #6 coal is in progress. As seen in Table 3, 12 to 42% of the tar sample collected was deposited on the filter as residue. Also, lower amounts of tar were collected for the lower rank Illinois #6 and Blue #1 coals than for the hva bituminous Pitt #8 coal. The tar yields seem somewhat lower than reported in the literature, indicating that some tar may have deposited in the sampling apparatus. Other investigators have corrected their measured yields for estimated deposition in the sampling apparatus[17]; this correction will be performed for these data in the future.

Table 2
^{13}C NMR Analysis of Coals, Tars, and Chars[a]

Coal	Sample	f_a	f_a^C	$f_{a'}$	f_a^H	f_a^N	f_a^P	f_a^S	f_a^B	f_{al}	f_{al}^H	f_{al}^*	f_{al}^O
Pitt #8	coal	65	3	62	23	39	5	16	18	35	24	11	7
Pitt #8	dis. tar	69	2	67	38	29	5	15	9	31	2	11	na
Pitt #8	tar res.	83	3	80	34	46	8	18	2	17	1	7	2
Pitt #8	char	81	5	76	24	52	6	18	28	19	11	8	6
Blue #1	coal	6	5	55	19	36	8	13	15	4	29	11	7
Blue #1	dis. tar	63	7	56	27	29	8	16	5	37	27	1	na
Blue #1	tar res.	72	6	66	24	42	9	15	18	28	17	11	12
Blue #1	char	77	5	72	24	48	9	2	19	23	15	8	4
Illinois #6	coal	66	3	63	21	42	7	16	19	34	24	1	8
Illinois #6	tar res.	8	6	74	28	46	8	18	2	2	12	8	3
Illinois #6	char	78	6	72	25	47	8	19	2	22	13	9	4

[a]Percentage carbon (error): f_a = total sp^2-hybridized carbon (±3); $f_{a'}$ = aromatic carbon (±4); f_a^C = carbonyl, $\delta > 165$ ppm (±2); f_a^H = aromatic with proton attachment (±3); f_a^N = nonprotonated aromatic (±3); f_a^P = phenolic or phenolic ether, δ = 150-165 ppm (±2); f_a^S = alkylated aromatic δ = 135-150 ppm(±3); f_a^B = aromatic bridgehead (±4); f_{al} = aliphatic carbon (±2); f_{al}^H = CH or CH_2 (±2); f_{al}^* = CH_3 or nonprotonated (±2); f_{al}^O = bonded to oxygen, δ = 50-90 ppm (±2).

Table 3
Derived Properties of Coal, Tar, and Char[b]

Coal	Sample	X_b	C_{cl}	σ+1	P_o	B.L.	S.C.	V (daf)	Tar (daf)	tar resid.
Pitt #8	coal	0.29	14	4.8	0.48	2.3	2.5			
Pitt #8	tar	0.134	8	2.4	0.45	1	1.4	46	22	
Pitt #8	tar res.	0.25	12	3.9	0.73	2.8	1.1	46	22	0.25
Pitt #8	char	0.368	18	5.7	0.67	3.8	1.9	42	19	
Blue #1	coal	0.27	13	5	0.48	2.4	2.6			
Blue #1	tar	0.09	7	3	0.58	1.7	1.3	23	6	
Blue #1	tar res.	0.273	13	4.7	0.54	2.5	2.2	23	6	0.12
Blue #1	char	0.264	13	5.2	0.72	3.7	1.5	29	7	
Illinois #6	coal	0.3	15	5.5	0.52	2.9	2.6			
Illinois #6	tar res.	0.27	13	4.6	0.69	3.2	1.4	32	6	0.42
Illinois #6	char	0.278	13	4.9	0.67	3.3	1.6	35	11	

[b]X_b = fraction of bridgehead carbons, C_{cl} = aromatic carbons per cluster, σ+1 = total attachments per cluster, P_o = fraction of attachments that are bridges, B.L. = bridges and loops per cluster, S.L. = side chains per cluster, V = total volatiles yield, Tar = tar collected on filters (not corrected for tar deposited in the sampling apparatus), tar resid. = fraction of collected tar that did not dissolve in CD_2Cl_2.

It is interesting to compare the NMR data for the tar, tar residue, and char with that of the coal. The carbon aromaticity $f_{a'}$ of the dissolved tar is similar to that of the parent coal, while that of the tar residue is generally higher (and close to that of the char). Perhaps the most interesting result is that the average cluster size of the dissolved tar is 7 to 8 aromatic carbons, which is much lower than the values of 12-18 found in the coal, tar residue, or char. Previous data on coals and

chars[21] also found that the number of aromatic carbons per cluster in coals and chars (ranging from lignite to lv bituminous coals) ranged from 10 to 18. The fact that the aromatic carbons per cluster in the tar residue is higher in the dissolved tar suggests a wide distribution of species with varying molecular weights in the tar.

The number of aromatic carbons per cluster in the tar residue is very similar to that found in the coal and char. The number of attachments per cluster in the dissolved tar is also significantly smaller than in the coal, while $\sigma+1$ in the tar residue is only slightly less than in the coal. The small number of attachments per cluster in the tars is also reflected in the values of bridges and loops per cluster (B.L.) and side chains per cluster (S.C.).

The average values of chemical structure features for the composite tar can be determined from combining the values for the dissolved tar and tar residue, according to the respective weight fraction of tar residue. This would raise the number of aromatic carbons per cluster in the tar to 8 and 9 for the two coals, which is still more than 35% lower than in the parent coal. It has been shown with repeated data sets that the number of aromatic carbons per cluster in the char does not increase substantially during devolatilization.[8-10, 21] The fact that C_{cl} in the tar is lower than in the coal, coupled with the fact that C_{cl} in the char remains constant at the same value as the coal, *can only be explained by ring breakage and not bridge breaking.* It is known that bond energies in aromatic rings are large, but it is suggested that the heteroatoms (largely oxygen and sulfur) in the clusters weaken the stability of the clusters. This is an interesting development, and suggests that the current view of devolatilization, as explained by current devolatilization models, may be in error.

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